

OXYGEN FUGACITY OF THE MARTIAN MANTLE FROM PYROXENE/MELT PARTITIONING OF REE. D. S. Musselwhite¹ and J. H. Jones², Astromaterials Research Office, NASA/JSC, Mail Code SR, Houston, TX 77058, ¹donald.s.musselwhite1@jsc.nasa.gov, ²john.h.jones1@jsc.nasa.gov.

Introduction: This study is part of an ongoing effort [1-3] to calibrate the pyroxene/melt REE oxybarometer for conditions relevant to the martian meteorites. Redox variations have been reported among the shergottites [4-6]. Wadhwa [4] used the Eu and Gd augite/melt partitioning experiments of [7], designed for the LEW86010 angrite, to infer a range of f_{O_2} for the shergottites. [5,6] inferred f_{O_2} using equilibria between Fe-Ti oxides. There is fairly good agreement between the Fe-Ti oxide determinations [5,6] and the estimates from Eu anomalies [4] in terms of which meteorites are more or less oxidized. The Eu anomaly technique and the Fe-Ti oxide technique both essentially show the same trend, with Shergotty and Zagami being the most oxidized and QUE94201 and DaG 476 being the most reduced. Thus, the variation in f_{O_2} appears to be both real and substantive.

However, although the redox trends indicated by the two techniques are similar, there is as much as a two log unit offset between the results of [5,6] and [4]. One explanation for this offset is that the Eu calibration used for the shergottites was actually designed for the LEW86010 angrite, a silica-undersaturated basalt whose pyroxene (diopside) compositions are rather extreme. To correct this, [1-3] have conducted experiments on the redox relationship of Eu partitioning relative to Sm and Gd for pyroxene/melt compositions more relevant to Martian meteorites. We report here preliminary results for experiments on pigeonite/melt partitioning as a function of f_{O_2} .

Experimental: Pigeonite/melt partitioning experiments were run in a gas-mixing DelTec furnace at f_{O_2} ranging from IW-2 to IW+4 (QFM+0.5). The simplified (i.e. CMAS + Fe, Na) starting composition was designed to produce a martian composition on the liquidus. This starting composition (Table1) was derived by mixing 65% glass from melting experiments on QUE 94201 [8] that is in equilibrium with the first pigeonite to crystallize, 30% of the experimental pigeonite (PX4), and 5% silica (to suppress olivine crystallization). This composition was doped with 1% each of Sm, Eu and Gd. Samples were suspended from a Re wire loop in the furnace. The samples were first raised to super liquidus temperature (1300°C) and held there for 30 minutes then ramped down at 1°/min. to run temperature (1240°C) and held for up to 24 hrs and then quenched in water. Run products were analysed for all elements with the SX100 EMP at NASA/JSC.

Table 1: Starting composition (Sh3)

Phase	PX4	QUE94201	Sh3
SiO ₂	53.24	50.30	51.78
Al ₂ O ₃	1.34	11.27	7.58
FeO	16.06	18.24	16.07
MgO	21.41	6.84	10.25
CaO	7.89	12.07	9.89
Na ₂ O	0.06	1.28	0.84
Eu ₂ O ₃			1.20
Gd ₂ O ₃			1.20
Sm ₂ O ₃			1.20

Results: The ratio of D_{Eu} to $D_{(Sm,Gd)}$ (pigeonite/melt) as a function of f_{O_2} derived from the current experiments is shown in Fig. 1.

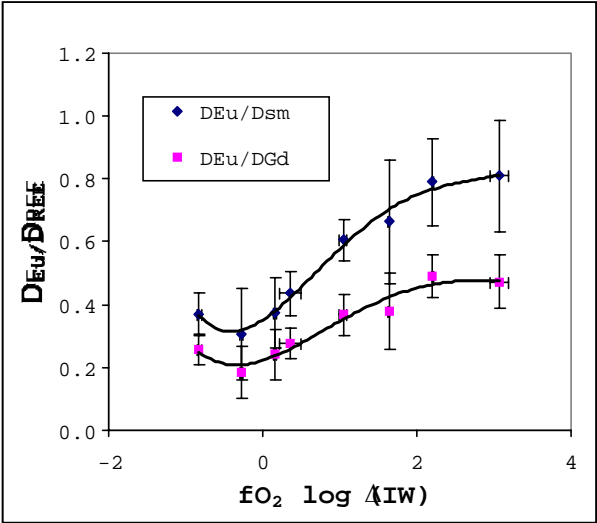


Fig. 1: Ratio of D_{Eu} to $D_{Sm,Gd}$ as a function of f_{O_2}

Discussion: From the new experimentally determined relationship between $(D_{Eu}/D_{Sm,Gd})_{pigeonite/melt}$ and f_{O_2} and published REE data for pigeonites [9] and whole rocks [4] we can estimate the f_{O_2} of the parental magmas of the basaltic shergottites. These f_{O_2} estimates can then be compared to f_{O_2} estimates from other methods – both Fe-Ti oxides and other pyroxene/melt REE oxybarometer calibrations. Fig. 2 is a plot of f_{O_2} determined from this study vs that from Fe-Ti oxides [5,6]. There is generally good agreement between the two methods with the f_{O_2} s deter

mined for Zagami, EET79,1(B), DaG 476 and QUE94201 agreeing within error. However, the fO_2 estimate for Shergotty from this study is quite a bit higher than for Fe-Ti oxides ($IW+4.6$ cf $IW+2.6$). We note that the calibration curve so far determined in this study is poorly determined at high fO_2 , so that with further results this discrepancy may disappear or diminish. The fO_2 for EET(A) from this study is also high compared with Fe-Ti oxides ($IW+3.5$ cf $IW+1.7$).

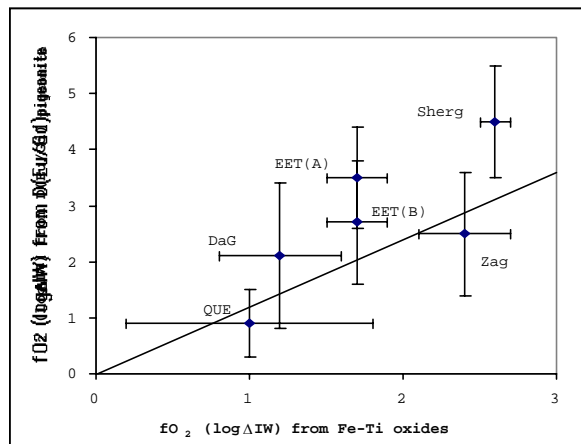


Fig.2: plot of fO_2 determined from this study vs that from Fe-Ti oxides [5,6]. Line plotted represents a 1:1 correspondence between the two methods.

Fig. 3 shows a plot of fO_2 determined from this study versus that from D_{Eu}/D_{Gd} for augite [1,2]. The correspondence between these two methods is poor, with the fO_2 determined from the augite method being 2 to 3 log units lower than for the pigeonite calibration. The reason for this discrepancy is not clear. As pointed out by [2], the use of augite for EET(A) (which has an almost 4 log unit discrepancy between the two methods) is likely not valid as augite is likely a late crystallizing phase in this meteorite. For Zagami, the whole-rock Gd value is poorly determined. In fact for all of the basaltic meteorites, the whole-rock Sm value is generally better determined than Gd. That being the case, for both the augite/melt and pigeonite/melt D ratio methods, the ratio D_{Eu}/D_{Sm} is preferred.

Fig. 4 shows a plot of fO_2 determined from this study versus that from D_{Eu}/D_{Gd} for pigeonite from an independent calibration [3]. As the same meteorite data was used in both cases, the discrepancy between the two is due entirely to differences in the calibration results.

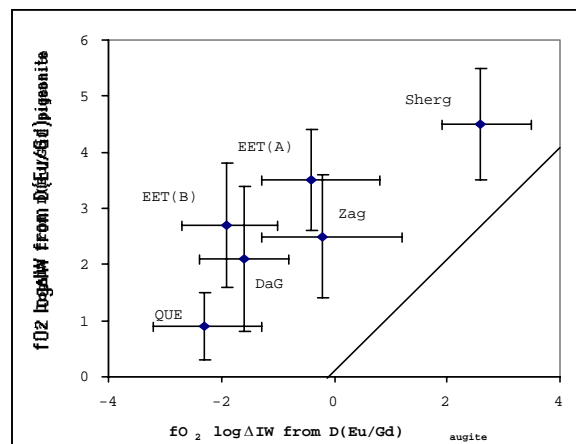


Fig.3: plot of fO_2 determined from this study vs that from D_{Eu}/D_{Gd} [1,2]. Line plotted represents a 1:1 correspondence between the two methods.

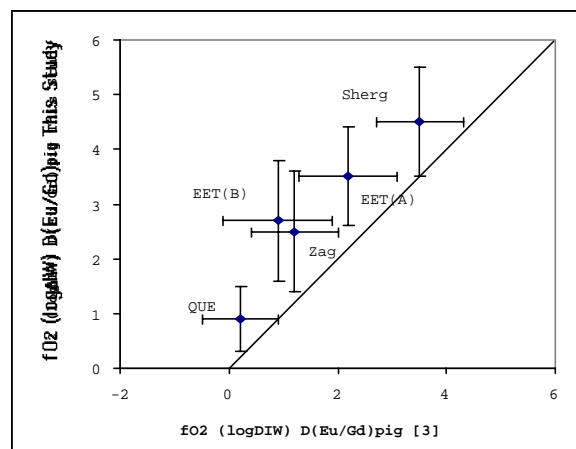


Fig.4: plot of fO_2 determined from this study vs that from D_{Eu}/D_{Gd} [1,2]. Line plotted represents a 1:1 correspondence between the two methods.

Further work: Further experimentation with the composition of this study need to be completed to refine the calibration. To further improve the determination of fO_2 in the basaltic shergottites, new, higher fidelity determinations of REE abundances (esp. Sm, Eu) in SNC pyroxenes is required.

References: [1] Musselwhite, D.S. and Jones J.H. (2002) *MAPS* 37, A101, [2] Musselwhite, D.S. and Wadhwa M. (2002) *SNC workshop*, Abstr. # 6024[3] McCanta M.C. and Rutherford, M.J. (2002) *SNC workshop*, Abstr. #6013. [4] Wadhwa, M. (2001) *Science* 291, 1527-1530. [5] Herd C. and Papike J.J. (2000) *MAPS* 35, A70. [6] Herd C. et al. (2001) *Geochim. Cosmochim. Acta* 66, 2025-2036. [7] McKay G.A et al. (1994) *Geochim. Cosmochim. Acta* 58, 2911-2919. [8] McKay, G., personal communication. [9] Wadhwa M. (2000) In *LPSC*. XXXI. #1966.